Co-synthesis of $LiFePO_4$ and Carbon Nanotubes

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The rate capabilities of $LiFePO_4$ composites are dependent on the structure of the carbon that coats the powders, formed during co-calcination with carbon-containing precursors.[1] The addition of readily decomposed pyromellitic acid[2] and graphitization catalysts such as ferrocene during synthesis results in coatings with low D/G (disordered/graphene) ratios, while maintaining the carbon content of the powders below 2 wt. %. This is important to avoid adversely affecting the tap density.[3] The good correlation between the pressed pellet conductivities of the $LiFePO_4$/C composites and their rate capability in lithium cells[4] is further confirmation of the importance of the carbon structure, because graphitic carbons generally have higher conductivities than disordered ones. [5]

Further examination of the pyrolysis of ferrocene/pyromellitic acid mixtures under conditions similar to those used for $LiFePO_4$ synthesis shows that multi-walled carbon nanotubes (MWCNTs, Figure 1) and graphite particles form, the amounts of which depend upon the Fe/C ratio.

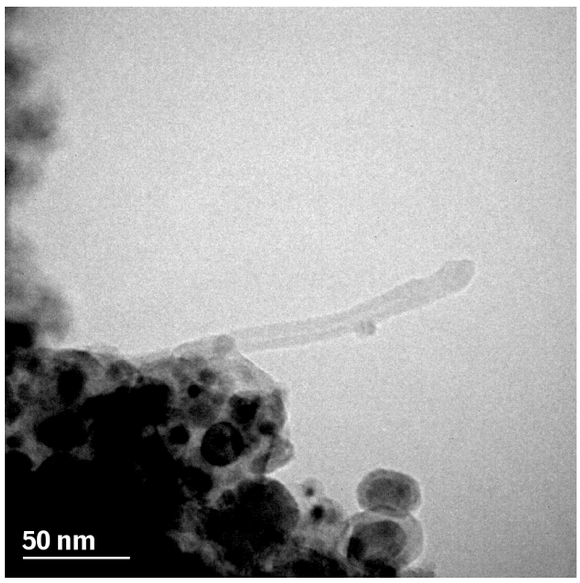

Figure 1. Image of a multiwalled nanotube formed during pyrolysis of ferrocene and pyromellitic acid at 700°C.

The presence of nanotubes in $LiFePO_4$ composites should allow substantial reduction of the amount of carbon black additive needed in composite electrodes, improving practical energy and power densities. The number of conductive particles needed to achieve the percolation threshold drops dramatically as aspect ratios increase, although other geometric factors such as curliness are also important.[6,7] For example, percolation thresholds as low as 0.1% have been reported for nanotubes in epoxy.[8] The co-synthesis of $LiFePO_4$ and carbon nanotubes potentially bypasses fabrication difficulties associated with mixing in pre-made nanotubes, alleviates health and safety concerns, and should reduce costs associated with purification.[9]

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References

1. M. M. Doeff, J. Wilcox, R. Kostecki, and G. Lau, *J. Power Sources,* in press (2006).
2. Y. Hu, M. M. Doeff, R. Kostecki, and R. Fiñones, *J. Electrochem. Soc.*, **151**, A1279 (2004).
3. Z. Chen and J. R. Dahn, *J. Electrochem. Soc.*, **149**, A1184 (2002).
4. J. Wilcox, M. M. Doeff, R. Kostecki, and M. Marcinek, manuscript in preparation.
5. R. Kostecki, B. Schnyder, D. Alliata, X. Song, K. Kinoshita, and R. Kötz, *Thin Solid Films,* **396**, 36(2001).
6. Y.-B. Yi and A. M. Sastry, *Proc. Royal Soc. London A*, **460**, 2353 (2004).
7. A. M. Sastry, personal discussion.
8. M. J. Biercuk , M. C. Llaguno, M. Radosavljevic, J. K. Hyun and A. T. Johnson., *Appl. Phys. Lett.* **80**, 2767 (2002).
9 . R. H. Baughman, A.A. Zakhidov, W. A. de Heer, *Science,* **297**, 787 (2002).